DEVELOP AND DEMONSTRATE MANUFACTURING PROCESSES FOR FABRICATING GRAPHITE FILAMENT REINFORCED POLYMIDE (Gr/PI) COMPOSITE STRUCTURAL ELEMENTS

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By

GENERAL DYNAMICS CONVAIR DIVISION
San Diego, California

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Hampton, Virginia

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DEVELOP AND DEMONSTRATE MANUFACTURING PROCESSES FOR FABRICATING GRAPHITE FILAMENT REINFORCED POLYIMIDE (Gr/PI) COMPOSITE STRUCTURAL ELEMENTS

V. A. Chase

Prepared by

GENERAL DYNAMICS CONVAIR DIVISION
San Diego, California

FOREWORD

The work reported herein was conducted by General Dynamics Convair Division, San Diego, California, under Contract NAS 1-14784. This is the third quarterly technical report covering contract activities for the period from 8 September 1977 to 8 December 1977. The program is sponsored by the NASA Langley Research Center, Hampton, Virginia. Mr. Edward L. Hoffman of the Manufacturing Technology Section, Materials Division is the NASA Technical Monitor.

At Convair the Program Manager is Mr. Vance A. Chase, material characterization is being conducted by Mr. E. S. Harrison, and fabrication process development is being performed by Mr. J. E. Hilzinger and Mr. Carl Smith. Adhesive bonding and honeycomb sandwich development is being conducted by Ms. V. Y. Steger.

V. A. Chase

Program Manager

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SECTION 1

INTRODUCTION AND BACKGROUND

One approach for increasing the efficiency of future reusable space vehicles involves the use of lightweight, elevated temperature resistant structural materials. One of the most promising materials for this application is graphite filament reinforced polyimide matrix composites. NASA's project Composites for Advanced Space Transportation Systems (CASTS) has been established to develop and demonstrate the technology required to achieve Gr/PI structural components with 316C (600F) operational capability.

The primary objective of this program, which is sponsored under the CASTS Project, is the development and demonstration of fabrication processes for graphite composites based on DuPont's NR-150B2 polyimide which are applicable to fabrication of large size structures. The program involves two major tasks and various subtasks:

TASK I - Process Development

(a) Material development and characterization for Quality Assurance.

(b) Laminate fabrication process development.

(c) Adhesive bonding study.

(d) Stiffened panel development.

(e) Honeycomb panel development.

(f) Chopped fiber molding process development.

(g) NDI development.

(h) Testing for process verification.

(i) Specifications.

TASK II - Demonstration Components

(a) Laminates

(b) Stiffened Panels

(c) Honeycomb Panels

(d) Chopped Fiber Moldings

(e) Structural Component

During the previous reporting periods,[1] studies were conducted to select a high strength graphite fiber having long term thermo-oxidative stability at 316C (600F). Weight loss measurements were made for graphite fibers and graphite/polyimide composites after thermal aging at 316C (600F) for times up to 1000 hours. Modmor II graphite fiber was selected for use on the contract based on thermal stability at 316C (600F), fiber strength properties, and the willingness of the fiber manufacturer to certify a maximum weight loss of 2% after 500 hours at 316C (600F). A weight loss of 0.76% was measured for the Modmor II fibers after 500-hour exposure times.

Also during the previous periods, it was determined that the ethyl alcohol solvent used in the NR-150B2 polyimide solution reacts with the 6F tetra acid monomer to form esters that are suspect of altering the materials composite fabrication processing characteristics. A decision was made to use prepreg based on NR-150B2/N-methyl-pyrrolidinone (NMP) solution.

Fabrication process development was conducted for laminates based on the initial order of Modmor II/NR-150B2-S4X (55% solids NMP resin solution) prepreg. The cure cycle previously developed at Convair for prepreg based on NR-150B2 (ETOH/NMP resin solution) provided excessive flow and resin starvation in the laminate. Studies were conducted into time/temperature hold condition before applying pressure for advancing the resin and reducing resin flow. A cure cycle, involving a two-hour hold

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[1] Quarterly Report #1 and #2, NAS1-14784.

at 149C (300F), was developed which gave a minimum resin flow and yielded laminates having a void content <2%. These laminates (C-9 and C-10) had less than optimum properties due to a low fiber volume and poor quality prepreg. The laminates had flexural strength of 1190 MN/m^2 (170 ksi) and 1141 MN/m^2 (163 ksi) at room temperature. Flexural strength at 316C (600F) for the two laminates was 833 MN/m^2 (119 ksi) and 945 MN/m^2 (135 ksi) for an elevated temperature strength retention of 70 and 83%.

Variation of the cure cycle that produced the low void laminates was investigated in an effort to obtain increased resin bleed and a higher fiber volume in the composite. No satisfactory cure cycle that gave resin bleed combined with low void content in the laminate was uncovered. These results suggested that a net resin (no-bleed) prepreg would be a promising approach for the NR-150B2 resin system.

It was determined that the 55% solids resin solution used for the initial batch of prepreg did not have sufficient viscosity to maintain good collimation of the fiber tows. The second prepreg batch, which was much improved, was based on 60% solids resin solution (NR-150B2-S5X) and 30 ±2% resin content. Delays were experienced in obtaining Modmor II fiber for the second batch of prepreg. To prevent schedule delays on the program, the second batch of prepreg was changed to Celion 3000 fiber. Fiber collimation and handling characteristics of this material were vastly improved over the initial prepreg batch.

The quality assurance tasks conducted previously include ultrasonic C-scan of laminates, infrared scanning study, and chemical and physical characterization of the prepreg and resin. Ultrasonic C-scans obtained on laminates C-9 and C-10 were equivalent to high quality graphite/epoxy composites.

SECTION 2

PROGRAM ACTIVITIES

2.1 SUMMARY

Prepreg based on 60% resin solids in NMP solvent (NR-150B2-S5X) and both Modmor II and Celion 3000 fiber was characterized for chemical and physical properties to provide quality assurance data. Small differences in chemical characteristics from the earlier material based on 55% resin solids solution were measured and were attributed to the increased time/temperature conditions required to achieve the higher resin solids solution.

The previously employed initial cure cycle (CR-4) to 204C (400F) gave very low void composites and essentially no resin bleed with the prepreg based on 60% resin solids solution. However, the dense, low-void composites presented a problem in postcuring the laminates without blistering. This is due to residual NMP solvent, which must diffuse through the dense resin at a rate sufficiently slow so as not to create internal pressure within the composite to cause blistering or delamination. A major activity during the reporting period has involved effort to develop a satisfactory postcure cycle.

During this reporting period Morganite Ltd. discontinued the manufacture of Modmor II graphite fiber, which had been selected earlier for use on this program. A decision was made to continue fabrication process development using Celion 3000 prepreg. A quantity of prepreg based on HTS-II fiber was ordered for evaluation as a candidate with the final fiber selection to be made at a later date.

2.2 PREPREG MATERIAL QUALITY ASSURANCE

A five pound batch of prepreg (Lot 6C-55) based on Modmor II fiber and 60% solids NR-150B2-S5X was received from Fiberite. This prepreg was prepared from the same resin batch used to prepare the Celion 3000 prepreg (Lot 6D-26) received earlier. Both batches of prepreg were based on 60% solids NMP resin solution and ordered with a 28% cured resin content to allow "no-bleed" curing. Actual resin contents tended to be >30% as measured by Convair. A 10-pound quantity of the Modmor II prepreg from Lot 6C-55 was delivered to NASA/LARC. Physical appearance and handling characteristics of the prepreg were very good. Properties and characteristics of the prepreg and resin are given in Table I. Properties for the initial batch of Modmor II prepreg based on 55% solids are included for comparison. Testing of the prepreg resin solution for viscosity versus temperature (Figure 1) gave a curve similar to that obtained for the 55% solution except that a higher viscosity was maintained across the temperature range. This can be attributed to the higher solids content. A minimum viscosity for the 60% solids solution was reached at ~121C (250F) where the 55% solids solution reached a minimum at ~88C (190F). For the higher solids material, higher temperature is required to achieve a solution (95C versus 75C) during the mixing operation. This apparently results in additional polymerization, which contributes to the higher viscosity. It appears reasonable that the difference in the viscosity curves can be attributed to the difference in solids content and degree of polymerization.

Acid and amine numbers were determined by chemical titration for the resin solution (combined Lots E14224-76 and E14224-78) with values of 1.55 and 0.789 meg./g. respectively being obtained. This compares to 1.68 and 0.864 meg./g. for the initial 55 solids solution resin batch (Lot E14224-34). The lower numbers for the high solids content resin batch support the assumption that polymerization reaction is occurring at the higher temperature (95C versus 75C) required for mixing the high solids solution. The acid/amine ratios for the initial and more recent resin batches are 1.94 and 1.97 respectively, showing reasonable agreement to the theoretical ratio of 2.0. Figures 2 and 3 are typical titration curves for the NR-150B2-S5X resin solutions.

TABLE I

PREPREG & RESIN DATA

Fiber Type	Modmor II	Celion 3000	Celion 3000	Modmor II
Prepreg Lot No.	6B-74	6D-26	6D-26	6C-55
Resin Lot No.	E14224-34	E14224-76 + E14224-78	⟶	⟶
Solvent(s)	NMP	NMP	NMP	NMP
DuPont Resin Solids (%)	55.3	60.4	60.4	60.4
Roll No.	2	1	2	1
Mfg. Date	5/20/77	8/23/77	8/23/77	9/1/77
Delivery Date	5/26/77	9/1/77	9/1/77	9/9/77
Resin Content, %				
Fiberite	44.6	28.1	27.4	33.2
Convair	36.9	32.5	34.0	32.9
Flow, %				
Fiberite	ND	25.2	25.8	24.1
Convair	22.0	22.1	22.4	21.6
Volatiles, %				
Fiberite	20.2	16.1	16.7	14.1
Convair	16.6	12.2	12.1	14.0
Roll Weight, kg (lb)	2.13(4.7)	2.49(5.5)	2.49(5.5)	2.58(5.7)
Width, cm (in.)	7.62(3.0)	7.62(3.0)	7.62(3.0)	7.62(3.0)
Drape	OK	OK	OK	OK
Tack	OK	OK	OK	OK
Gel Time (min.)				
Fiberite at 204C (400F)	-	1.5	1.3	-
Convair at 204C (400F)	0.6	1.0	-	0.9
Fiberite at 177C (350F)	5.1	4.4	3.5	3.8
Convair at 177C (350F)	2.5	3.0	-	2.9
Fiberite at 149C (300F)	-	11.4	11.0	-
Convair at 149C (300F)	7.5	4.2	-	4.5
Process Gel Temp., C (F)	140.6(285)	171(340)	171(340)	171(340)
Areal Weight, gm/ft^2	21.44	22.58	25.83	25.0

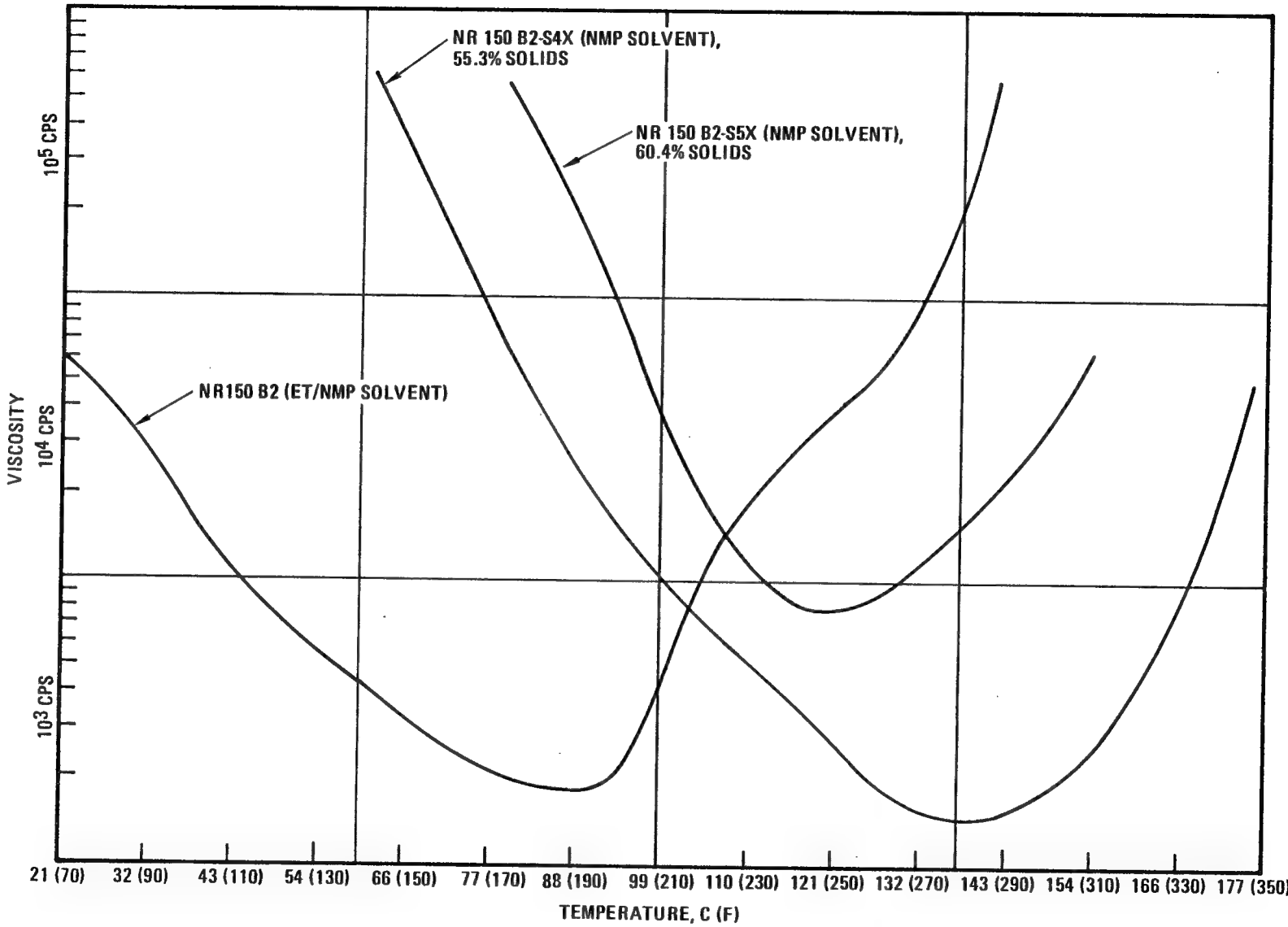


Figure 1. Viscosity Versus Temperature for NR-150B2 Solutions

High pressure liquid chromatograph (HPLC) studies were conducted on the 60% solids resin lot used for the recent batches of prepreg and compared to the earlier 55% solids resin lot (Figures 4 and 5). A scan was also run on the earlier NMP/EtOH based NR-150B2 as a matter of interest (Figure 6). Our initial efforts have been centered on reverse phase/gradient elution techniques using a water/methanol mix (40-80%) as the eluting solvent and indicate minor differences between the 55% and 60% resin solids

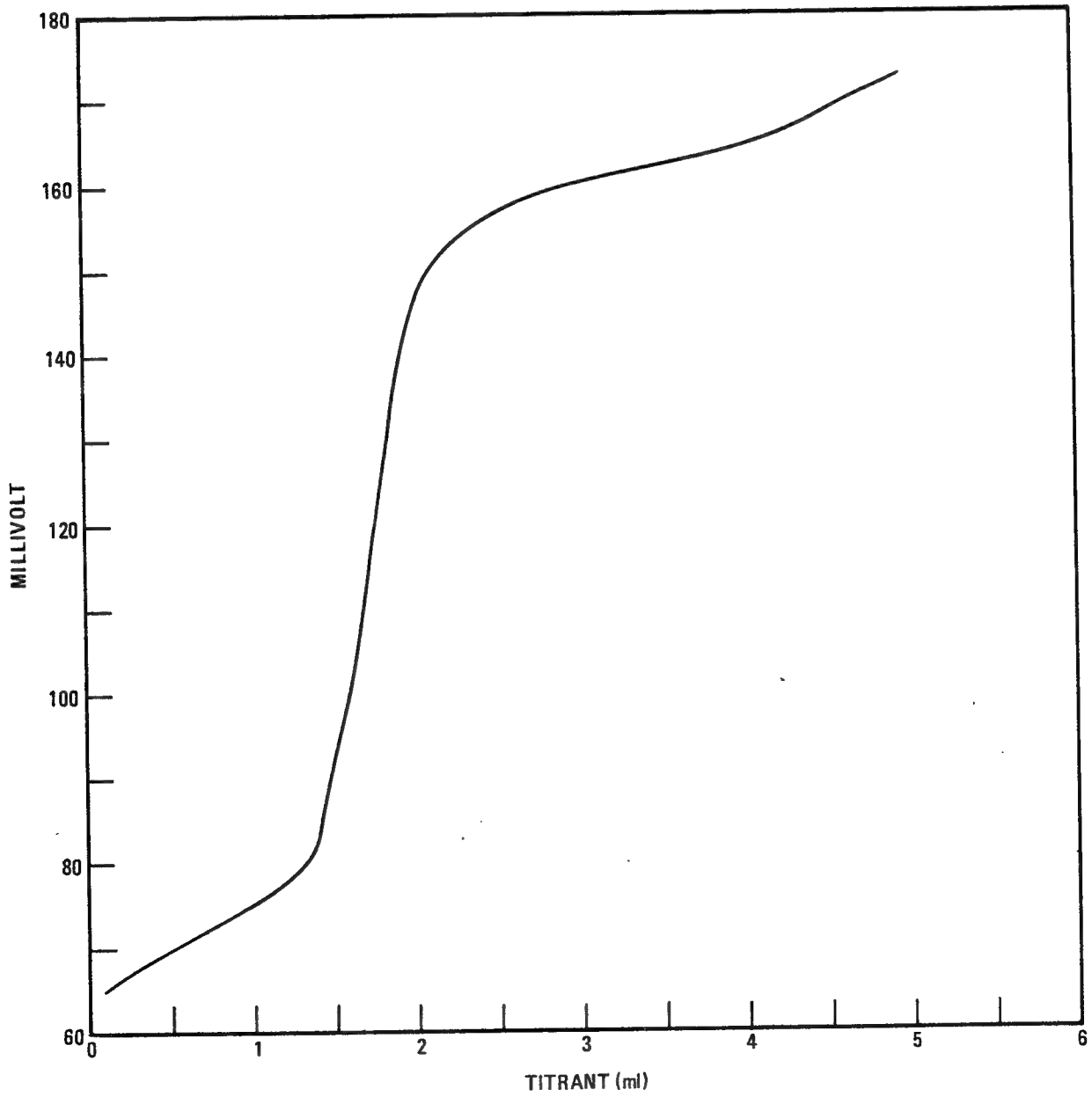


Figure 2. Acid Titration Curve for NR-150B2-S5X Resin Solution (Combined Batches E14224-76 and E14224-78)

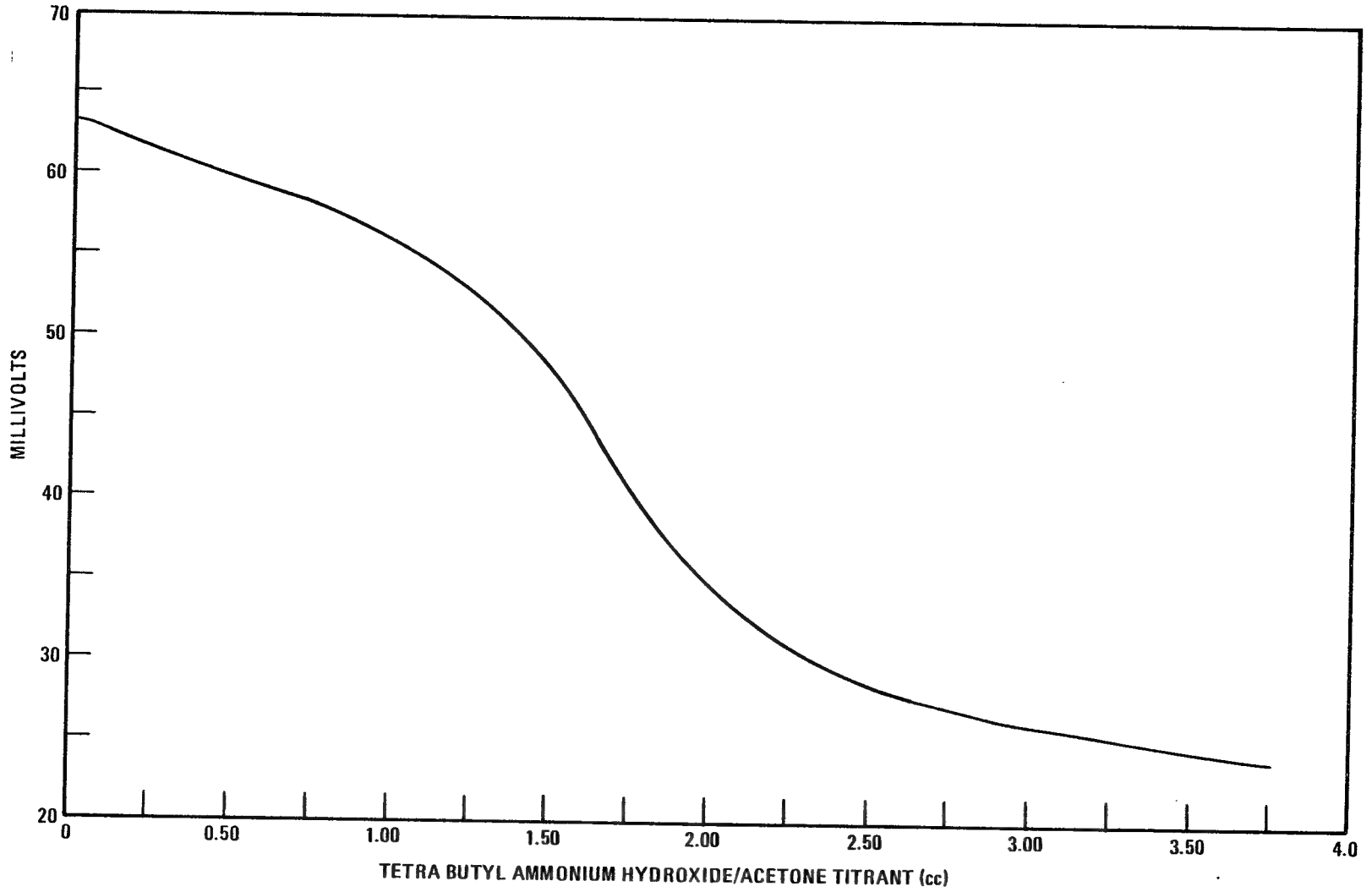


Figure 3. Amine Titration Curve for NR-150B2-S5X Resin Solution (Combined Batches E14224-76 and E14224-78)

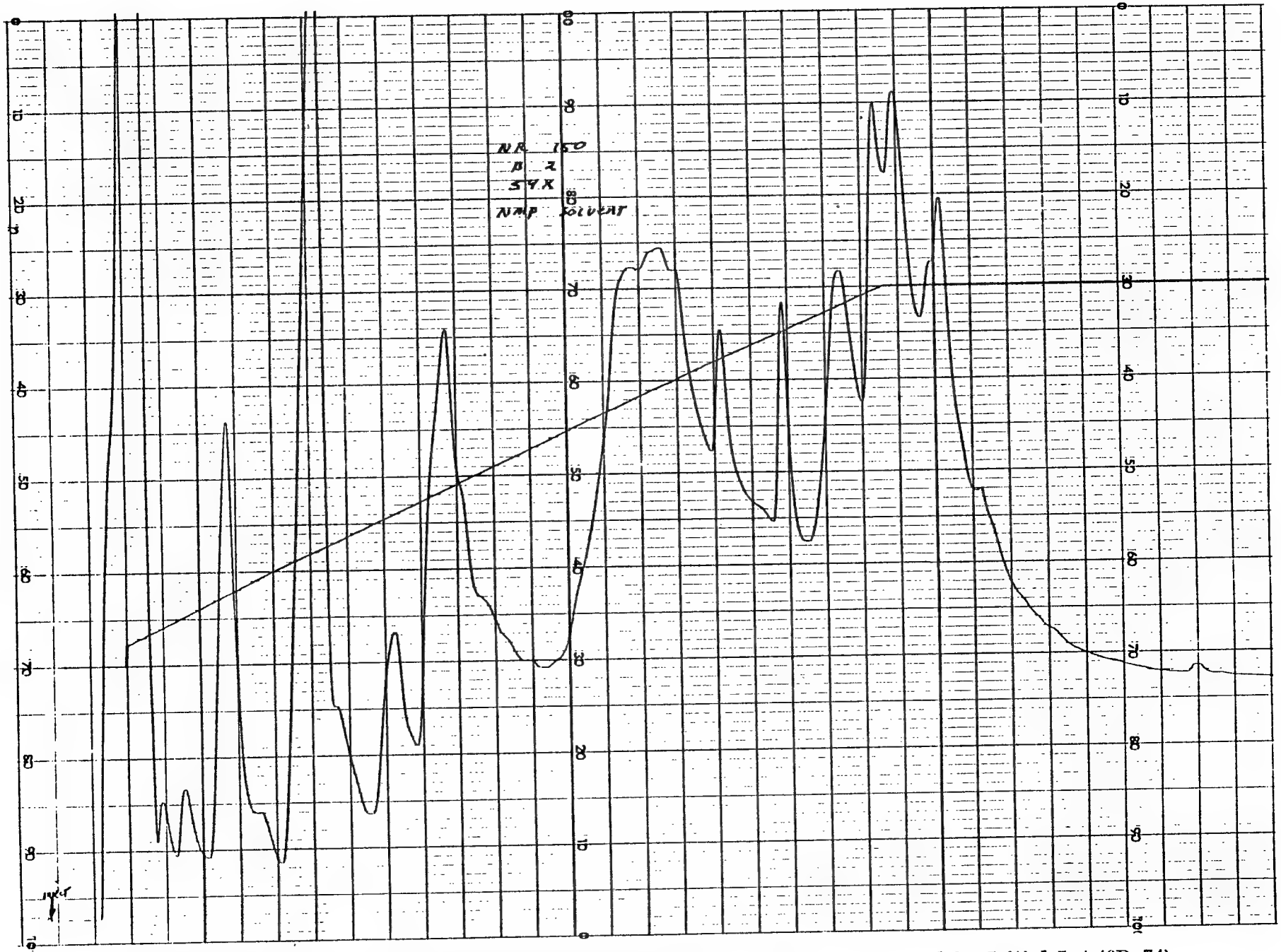


Figure 4. H.P.L.C. Scan for NR-150-B2-S5X Resin Solution (55% in NMP) Used for Initial Lot (6B-74) of Modmor II Prepreg

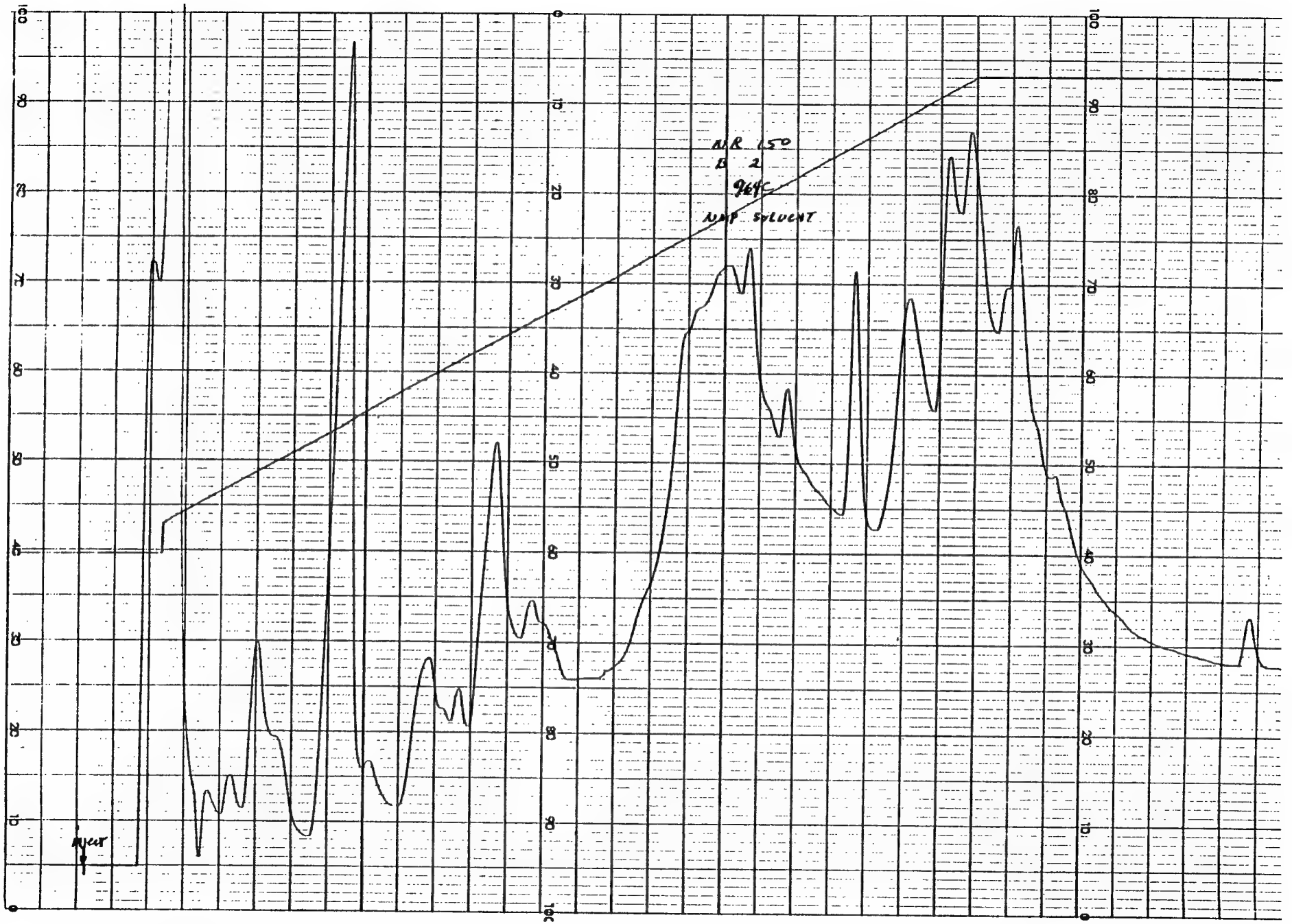


Figure 5. H.P.L.C. Scan for NR-150-B2-S5X Resin Solution (60% Solids in NMP) Used for Recent Lots of Celion 3000 (Lot 6D-26) and Modmor II (Lot 6C-55)

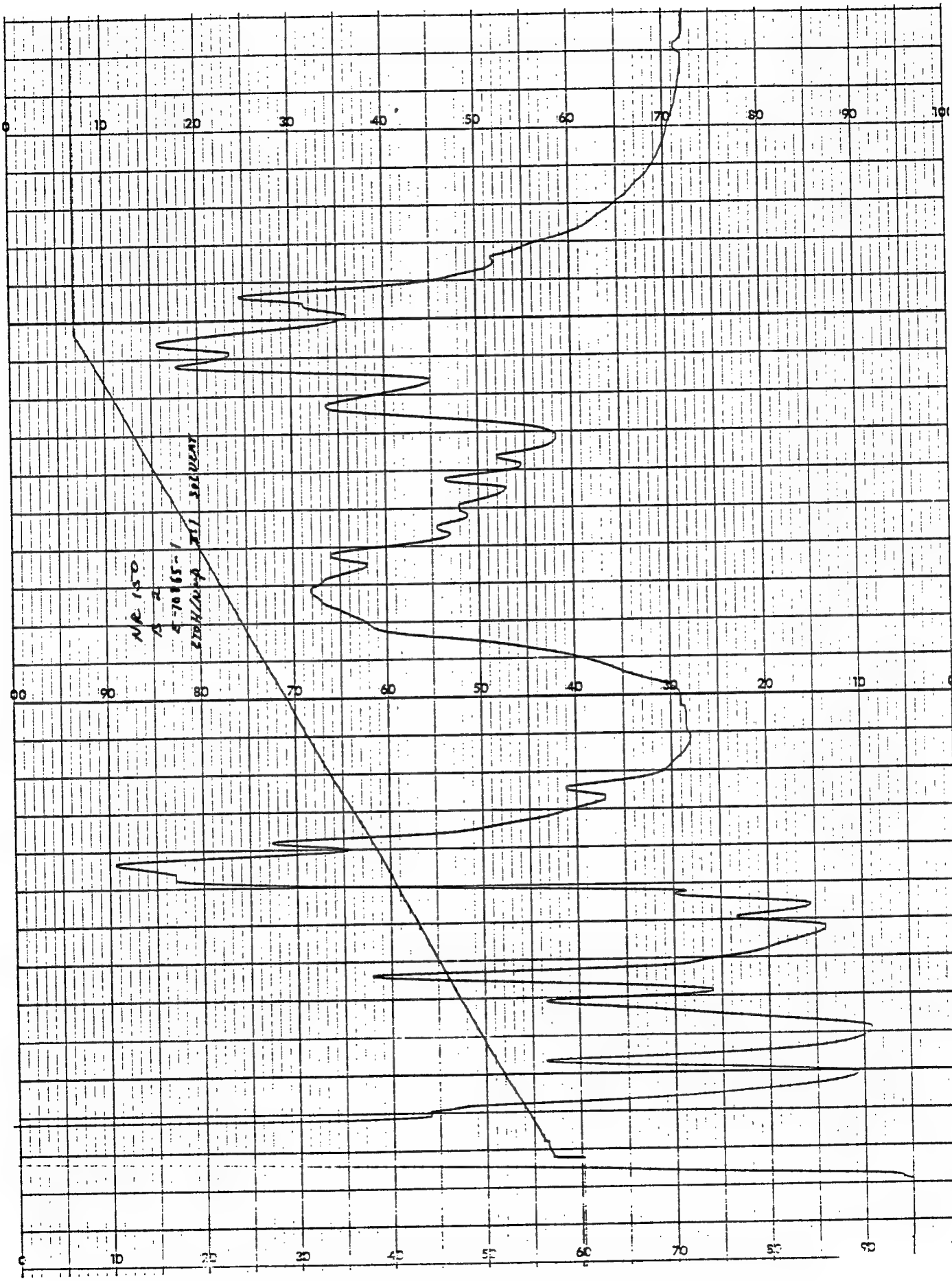


Figure 6. H.P.L.C Scan for NR-150B2 Based on ETOH/NMP Solvent

solutions over anticipated concentration dependency. Monomers will be obtained from DuPont or by isolating from the resin solution for use in spiking studies to identify the monomer peaks.

2.3 FABRICATION PROCESS DEVELOPMENT

Earlier studies established the need for a temperature hold at 149C (300F) for the NR-150B2 prepreg material to increase the viscosity sufficiently to prevent excessive resin flow when vacuum bag/autoclave pressure is applied. An investigation was also conducted into the possibility of performing the 149C (300F) advancement step for the NR-150B2 initial cure in an oven rather than the autoclave. Laminates C-28, C-29, and C-30 (Celion 3000) were vacuum bagged without bleeder and advanced in an oven at 149C (300F) for 1, 2, and 3 hours respectively. After removal from the oven, they were rebagged with bleeder and subjected to the standard initial C-4 autoclave cure shown below without the 149C (300F) hold (Steps 1 and 2). The laminates exhibited no bleed during the initial cure and visually appear to be of good quality.

Standard NR-150B2 Autoclave Cure Schedule

Initial Cure (CR-4)

(1) Without vacuum heat at 1C (1.8F) min. to 149C (300F) and hold one hour.

(2) Apply full vacuum and hold one additional hour at 149C (300F).

(3) Heat to 185C (365F) at 1C (1.8F)/minute.

(4) Hold one hour at 185C (365F).

(5) Apply 1400 kN/m^2 (200 psi) while heating to 204C (400F) at 1C (1.8F)/minute.

(6) Hold two hours at 204C (400F).

(7) Cool to 65C (150F) under pressure.

Postcure

(1) Apply full vacuum and heat to 316C (600F) at 1.1C (2F)/minute.

(2) Apply 1400 kN/m^2 (200 psi) at 177C (350F).

(3) Hold one hour each at 316, 343, and 371C (600, 650, and 700F).

(4) Raise to 399C (750F) and hold for five hours.

Laminate C-31 (Celion 3000) involved an evaluation of the possibility of performing the 149C (300F) advancement step in an oven while unrestrained (no vacuum bag). However, excessive swelling and distortion of the layup was experienced. This distortion along with the extreme boardness of the layup after advancement made it impractical to cure laminate C-31 (Figure 7).

Postcure of Laminates C-28, C-29, and C-30 was conducted in accordance with the above postcure schedule. Upon removal from the autoclave, the laminates were found to have developed blisters obvious from visual examination. The laminates were inspected by ultrasonic C-scan at 5 MHz and different gain settings (Figures 8, 9 and 10). At the lower gain settings the blisters tend to blend in and become obscured by what is assumed to be porosity; however, at higher gain setting, they are very distinct. Flexural, short beam shear and specific gravity specimens were cut from the

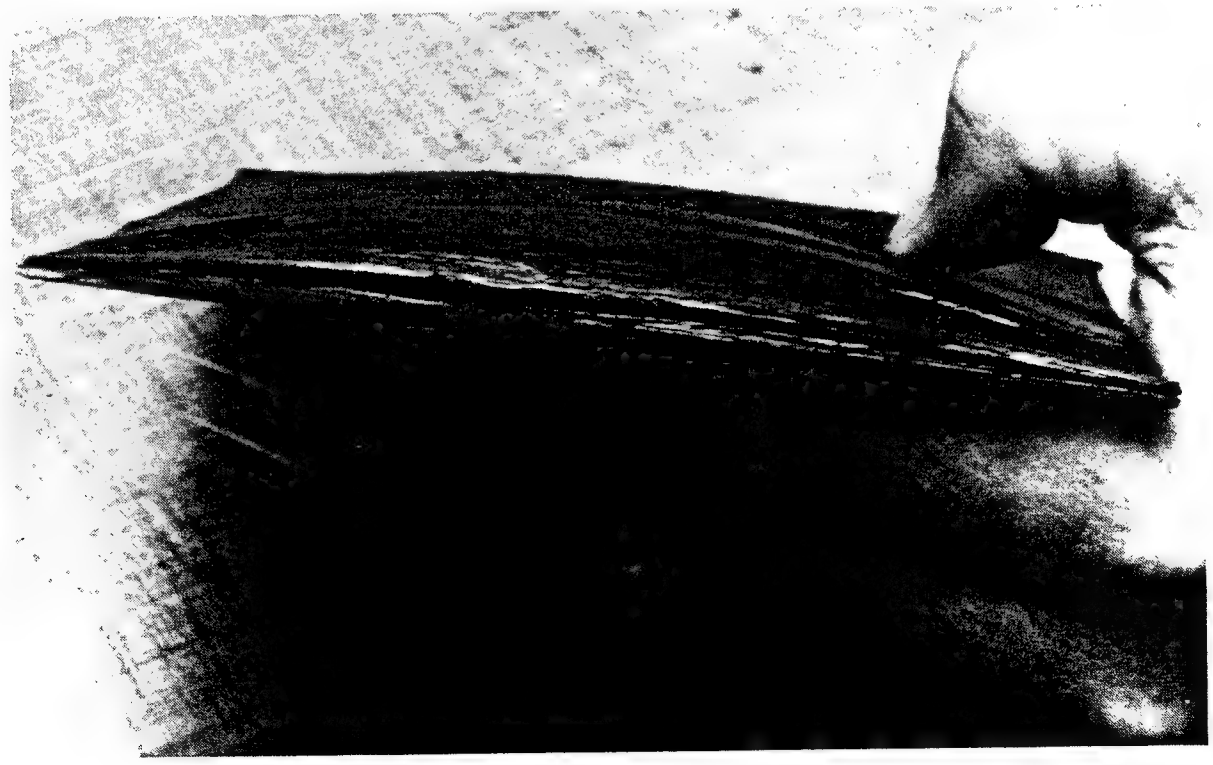


Figure 7. Laminate C-41 After Advancement in Oven at 149C (300F)

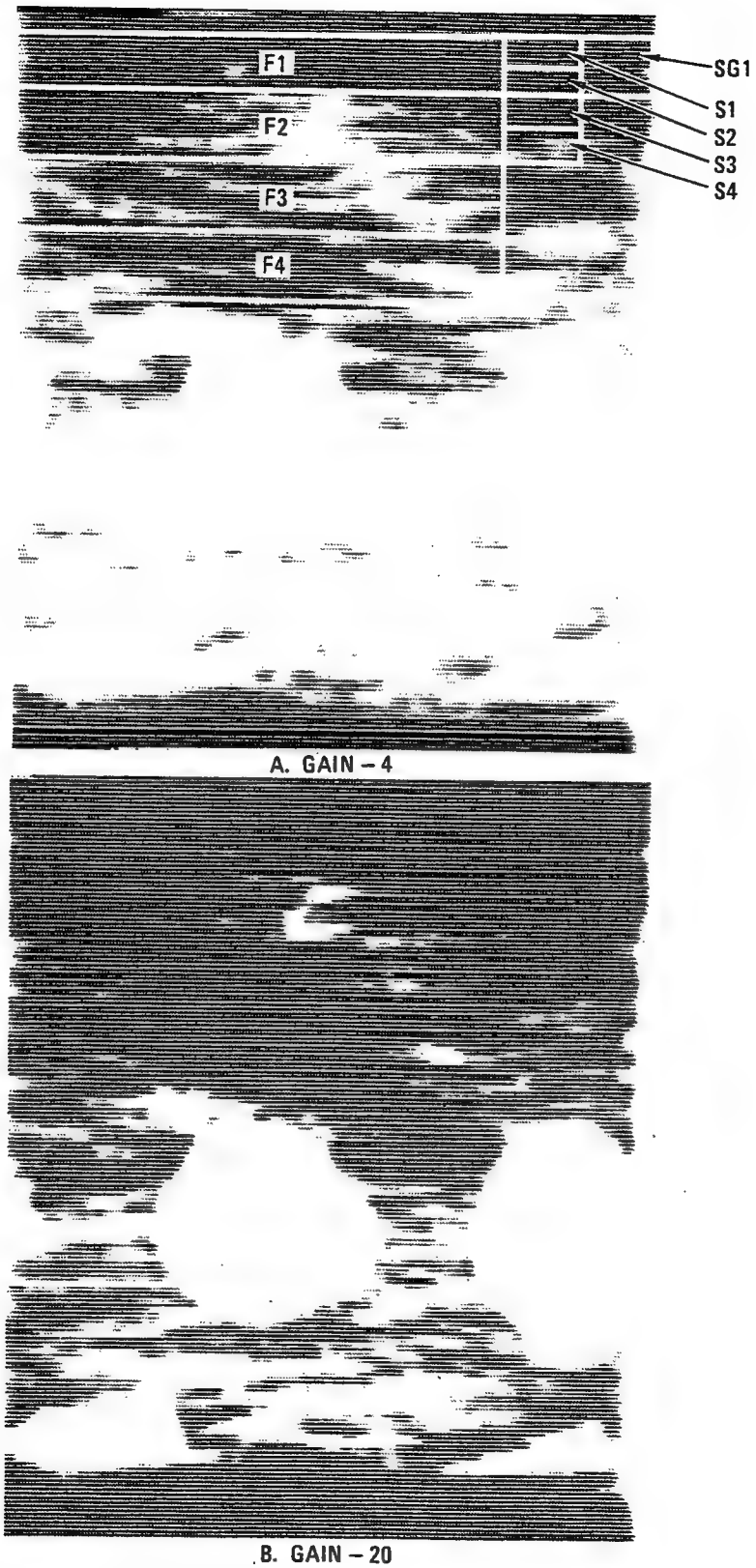
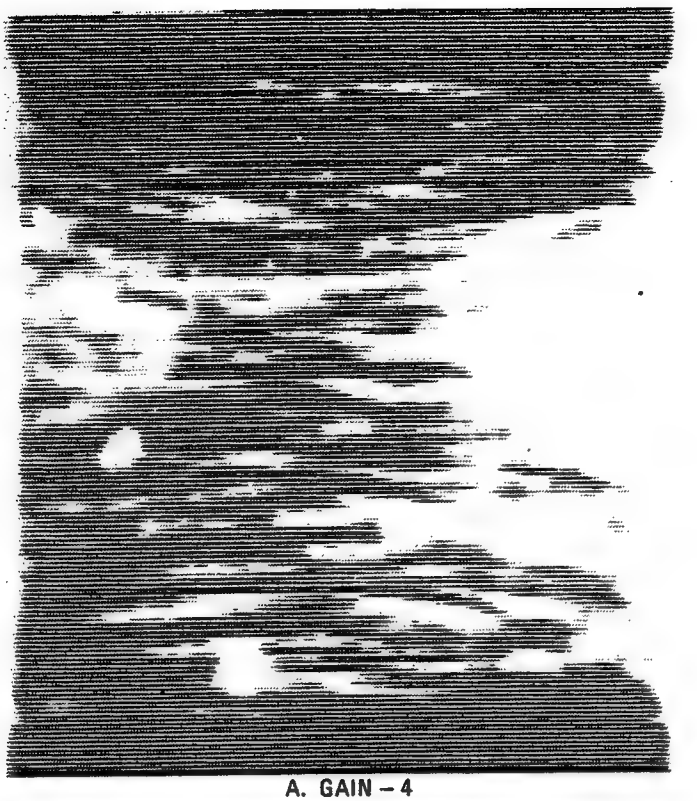
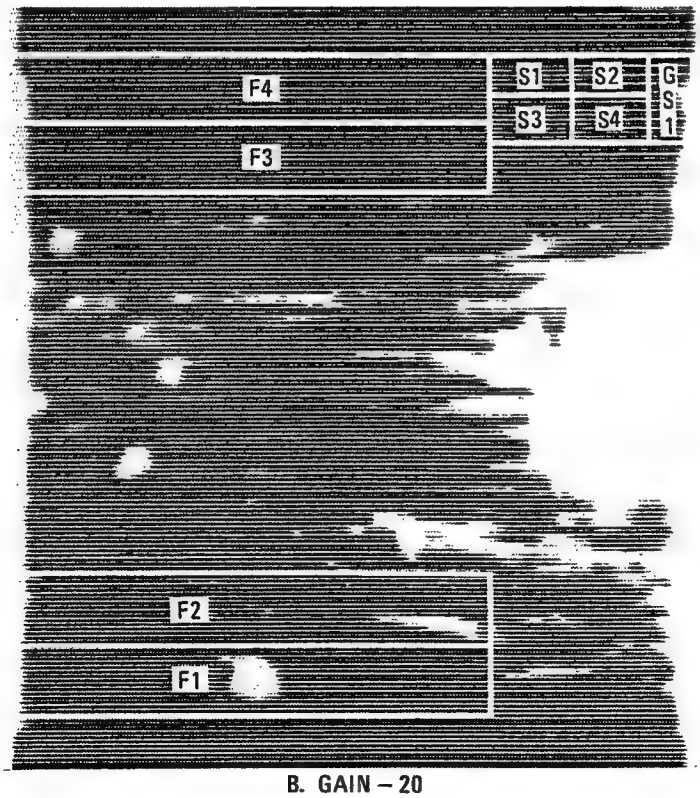


Figure 8. Ultrasonic C-Scan (5 MHz) and Specimen Cutting Pattern for Laminate C-28

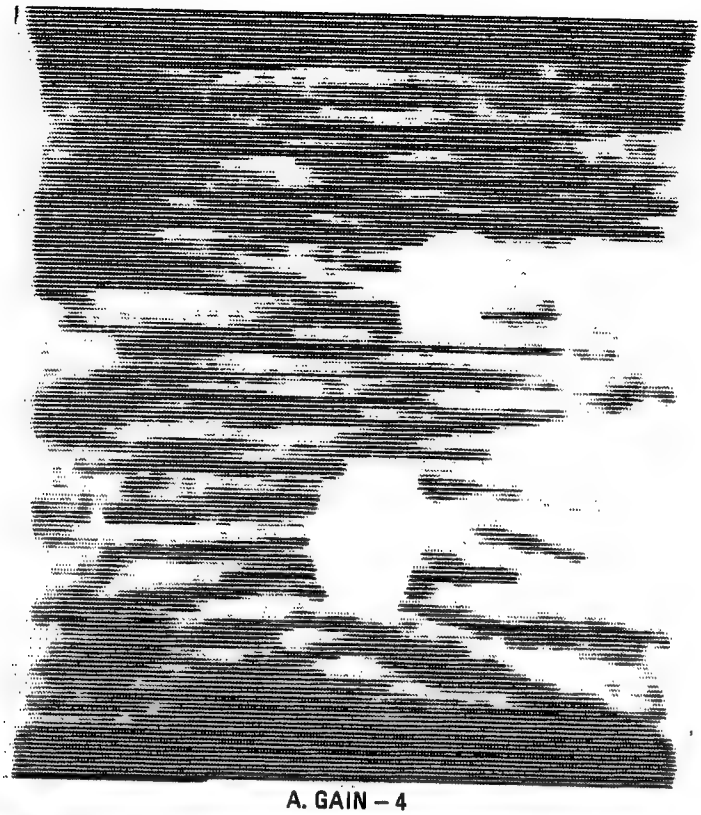


A. GAIN – 4

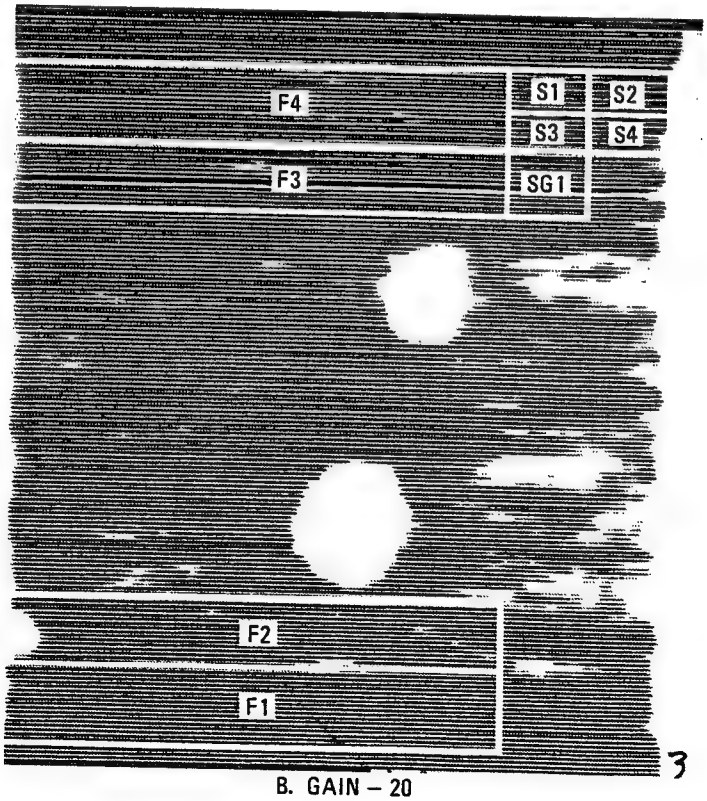


B. GAIN – 20

Figure 9. Ultrasonic C-Scan (5 MHz) and Specimen Cutting Pattern for Laminate C-29



A. GAIN – 4



B. GAIN – 20

Figure 10. Ultrasonic C-Scan (5 MHz) and Specimen Cutting Pattern for Laminate C-30

laminates as shown in Figures 8, 9, and 10. Even though all three laminates had calculated void contents on the order of 6%, average RT flexural strength values ranged from 1631 to 1771 MN/m^2 (233 to 253 ksi) and SBSS ranged from 90.3 to 97.3 MN/m^2 (12.9 to 13.9 ksi) (Table II).

Laminates C-32 (Celion 3000) and C-33 (Modmor II) were prepared using the C-4 initial cure and postcured by the standard postcure schedule. Again, blistering was evident after postcure. Ultrasonic C-scans were conducted on these laminates at 5 MHz and at various gain settings. These are shown in Figures 11 and 12. Specimens were cut from the sound areas of laminates C-32 and C-33 and tested for flexural strength, SBSS, fiber volume, specific gravity, and void content. RT flex values of 1890 and 1386 MN/m^2 (270 and 198 ksi) respectively were measured for laminates C-32 (Celion 3000) and C-33 (Modmor II) and represent the highest values obtained for these materials to date. Also void content for both laminates was < 1% in areas that had not blistered.

Also postcured with laminates C-32 and C-33 was a large 15 by 15 by 1/8 inch (CD-1) unidirectional Modmor II laminate. This laminate was prepared to demonstrate scale-up from the typical 6 by 6 inch laminates used throughout the program for process development and for evaluation of thermophysical properties under a separate NASA/LaRC program. This laminate did not exhibit any visual signs of blistering; however, ultrasonic C-scan indicated delamination and porosity (Figure 13).

An additional set of Celion 3000 and Modmor II laminates (C-34 and C-35) were fabricated and postcured by the standard cycle with blistering occurring for both laminates. Figure 14 illustrates the type of blistering experienced with the blistered area being greatly increased in thickness over the sound portion of the laminate.

Both laminates show approximately 12% weight loss during initial cure and total weight losses of 18.7 to approximately 20.1% after final postcure. Neither layup

TABLE II

PROPERTIES FOR NR-150B2-S5X GRAPHITE/POLYIMIDE COMPOSITE C-28 TO C-33 (12 PLY, 0°)

Laminate No.	C-28	C-29	C-30	C-32	C-33
Fiber	Celion 3000	Celion 3000	Celion 3000	Celion 3000	Modmor II
Cure	C-4(1)	C-4(1)	C-4(1)	C-4	C-4
Postcure	STD	STD	STD	STD	STD
Flexural Strength MN/m^2 (ksi)					
RT	1631 (233)	1645 (235)	1771 (253)	1890 (270)	1386 (198)
316C (600F)	763 (109)	980 (140)	756 (108)	238 (134)	714 (102)
Short Beam Shear Strength MN/m^2 (ksi)					
RT	97.3 (13.9)	90.3 (12.9)	89.6 (12.8)	105.7 (15.1)	49.7 (7.1)
316C (600F)	38.5 (5.5)	38.5 (5.5)	39.9 (5.7)	38.5 (5.5)	(ND)
Specific Gravity	1.54	1.55	1.55	1.60	1.55
Fiber Content, % Wgt.	71.9	71.5	77.4	64.6	60.5
% Volume	67.0	66.6	73.1	59.2	56.4
Cured Ply Thickness, mm (mil)	.160 (6.3)	.150 (5.9)	.145 (5.7)	.130 (5.1)	.152 (6.0)
Glass Transition Temp., C	356	359	356	357	358
Void, %	6.2	5.5	6.8	.8	0

(1) After Vacuum Bag/Oven B-Staging

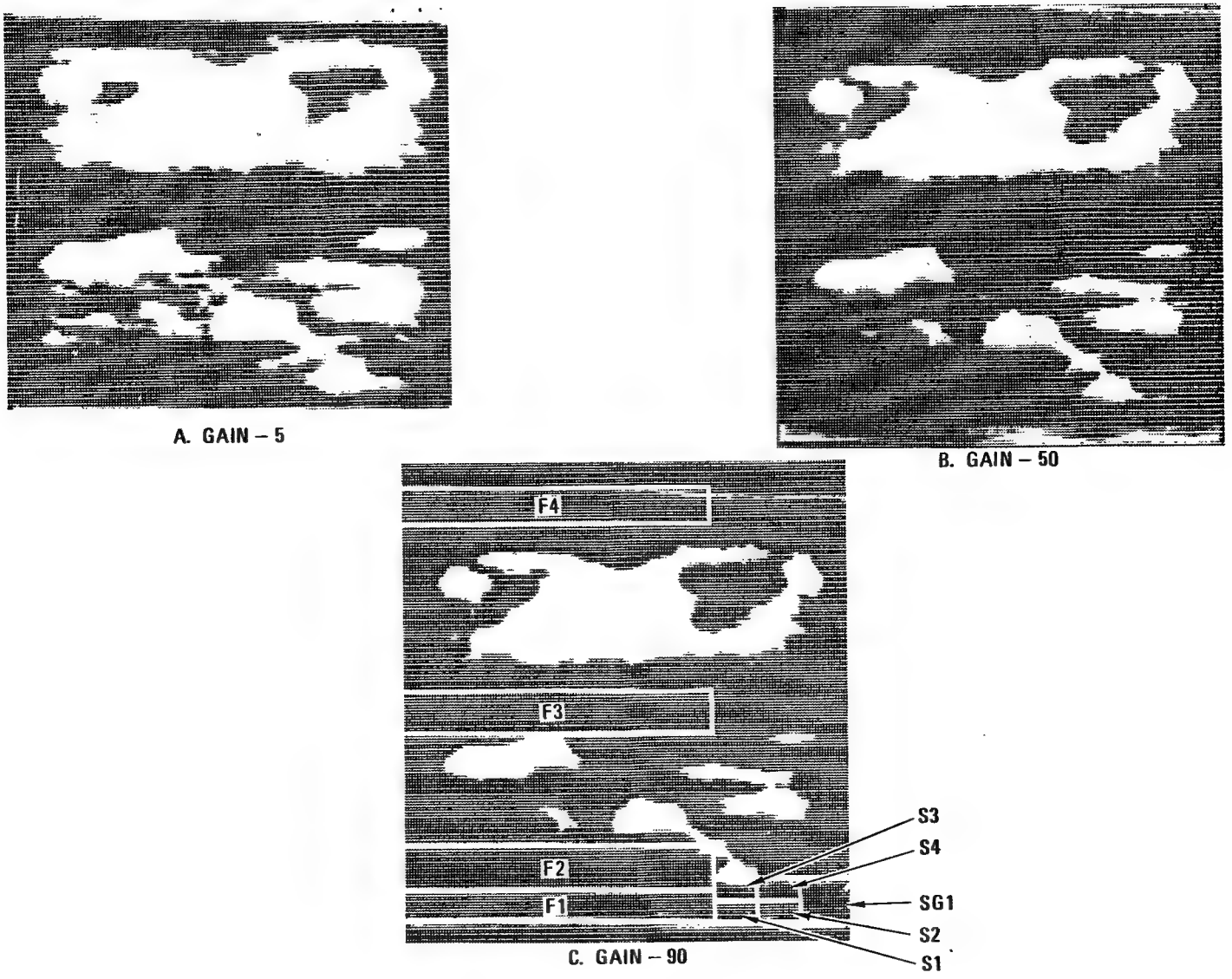


Figure 11. Ultrasonic C-Scan (5 MHz) and Specimen Cutting Pattern for Laminate C-32

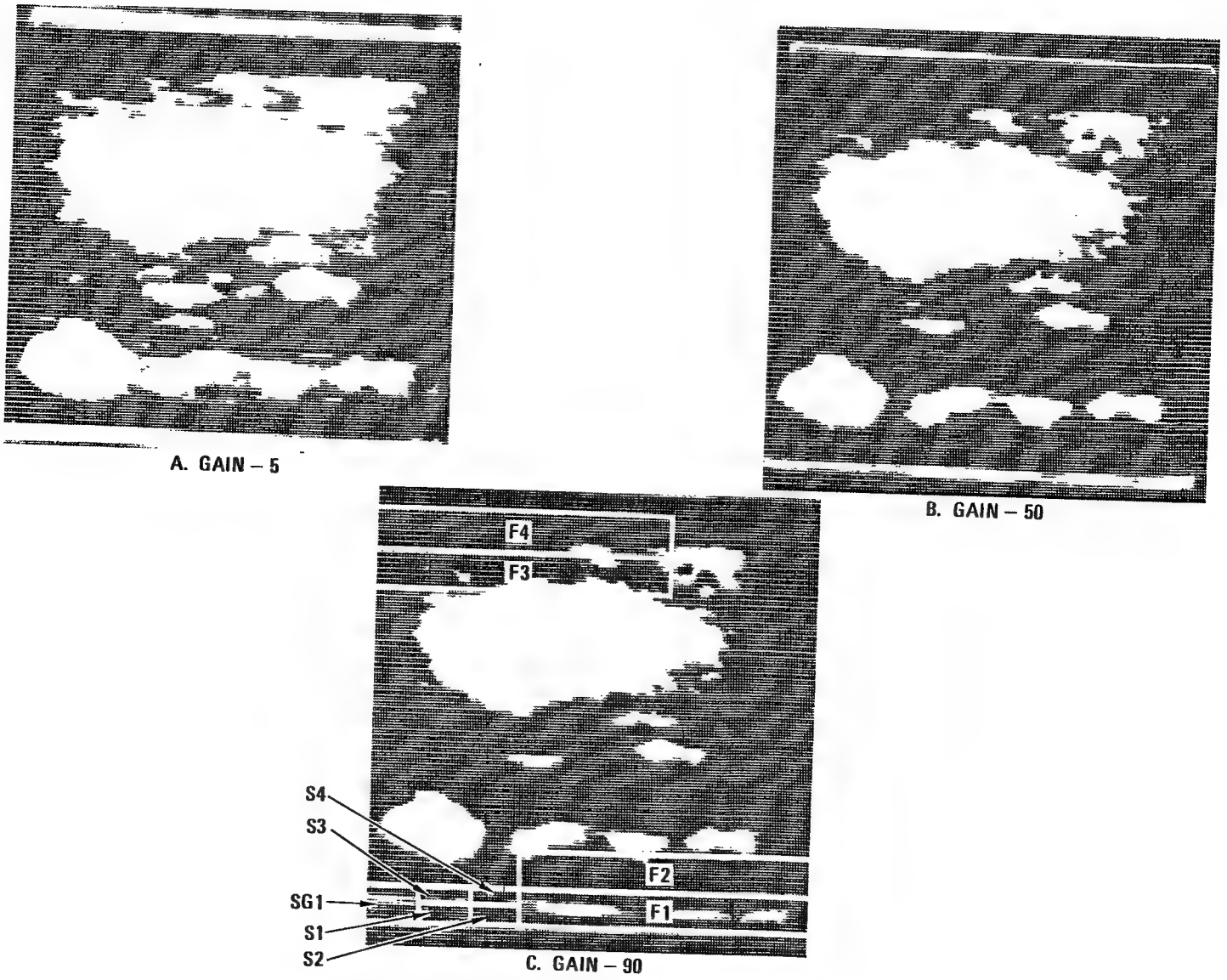
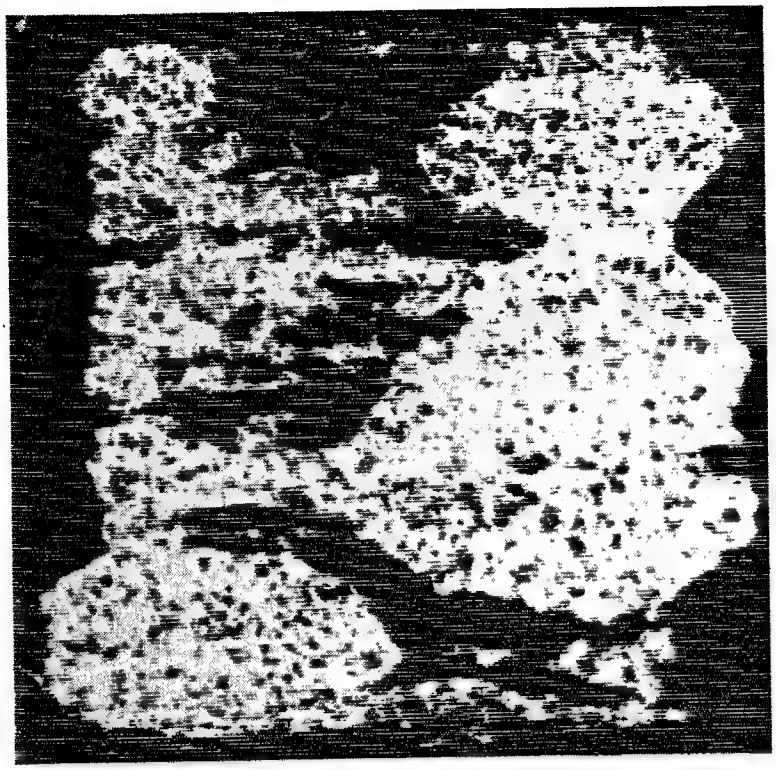
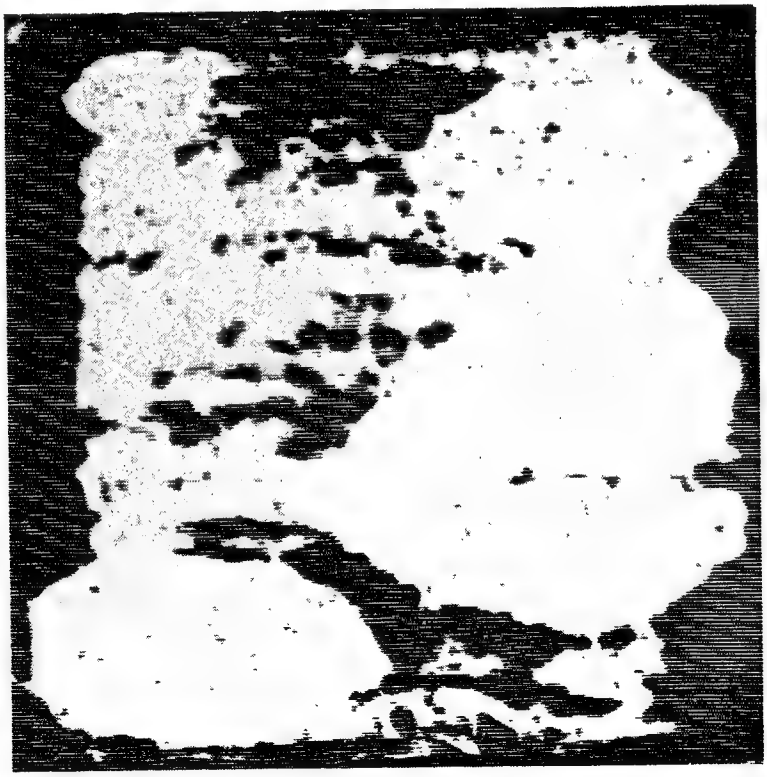


Figure 12. Ultrasonic C-Scan (5 MHz) and Specimen Cutting Pattern for Laminate C-33



A. GAIN 1.4



B. GAIN 1.0

Figure 13. Ultrasonic C-Scan for 15 by 15 by 1/8-Inch NR-15DB2/Modmor II/ Laminate (CD-1) at 1 MHz

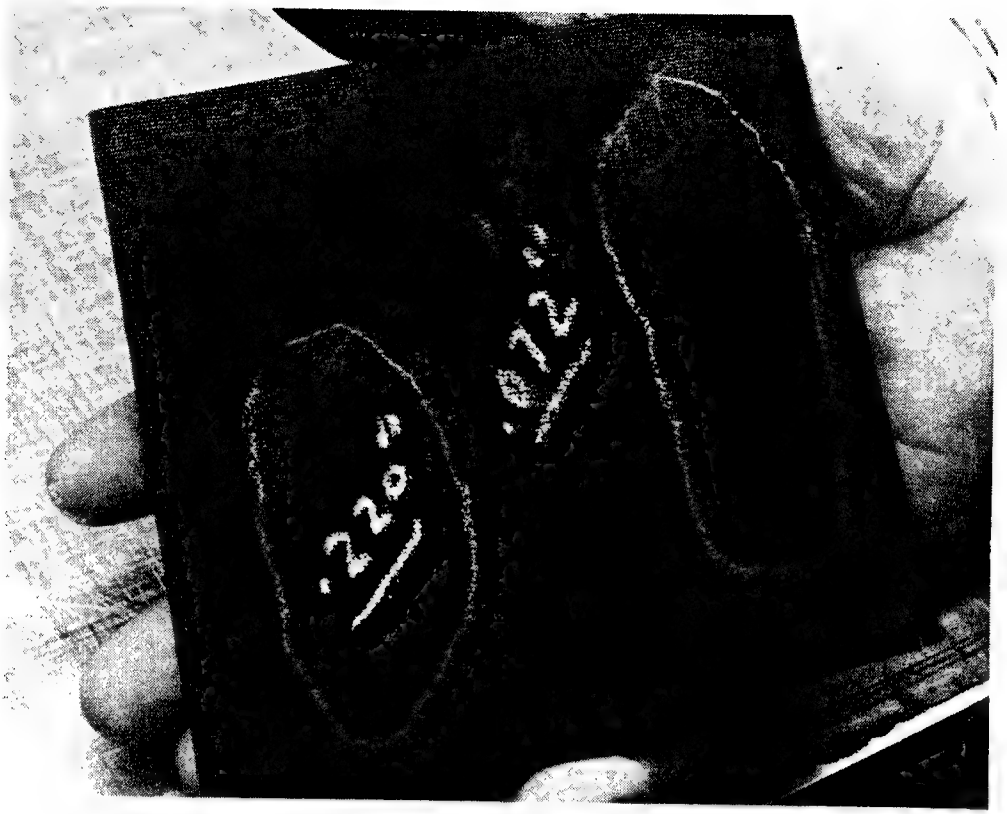


Figure 14. Typical Visual Blistering of NR-150 Lamination

exhibited flow during cure, with only minimum bleeder stain, and 6.6 to 8.5% volatiles remained to be removed during the postcure. By contract, earlier dense laminates showed a weight loss of 10 to 12% (C9 and C10) during postcure and did not blister. Apparently the volatile removal was reasonably complete since glass transition temperatures (Tg) exceeding 350C were measured. No further testing was done on laminates C-34 and C-35.

At this point a detailed analysis was conducted of the fabrication process in an effort to solve the laminate blistering problem. This analysis disclosed that the vacuum bag had presented problems of leakage during the 399C (750F) postcure on earlier laminates, which was alleviated by reducing the autoclave pressure. As a result the laboratory technicians had established a "standard procedure" of reducing the autoclave pressure from 1400 kN/m^2 (200 psi) to 350 kN/m^2 (50 psi) when the 399C (750F) postcure step was reached. When the autoclave pressure was released at 399C (750F) the laminate was above its Tg and contained residual NMP, which created sufficient

internal pressure to cause blistering. It appeared logical that maintaining autoclave pressure throughout the postcure would alleviate the blister problem.

Laminates C-36 and C-37 were cured using the CR-4 initial cure schedule for evaluation of the effect of maintaining full autoclave pressure during postcure. Inadvertently, full vacuum was applied too early in the cure cycle causing very high resin flow and resin starved laminate condition. These laminates were replaced by C-38 and C-39.

Laminate C-38 was used to evaluate the effect of 1400 kN/m^2 (200 psi) pressure throughout the postcure cycle. Upon removal from postcure the laminate appeared sound. However, ultrasonic C-scan and physical and mechanical properties measurement showed the laminate to be delaminated and/or contains interal porosity (Figure 15, Tables III, IV, and V). The high-pressure postcure was sufficient to prevent visual blistering, but the rate of temperature increase was apparently high enough to create internal pressure from the residual solvent and result in delamination.

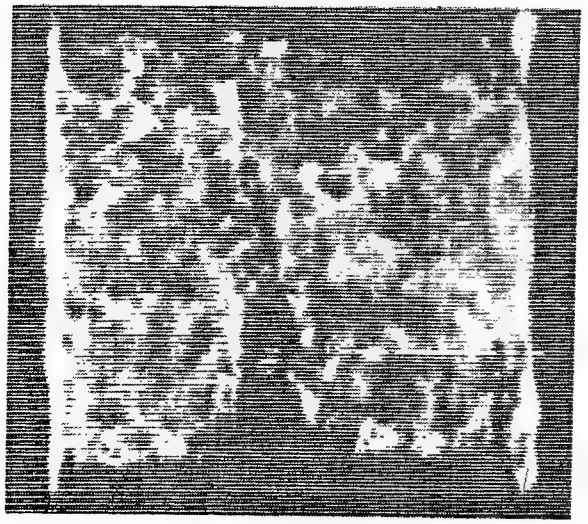
At this time an attempt was made to study volatile weight loss by TGA during postcure. Figure 16 is a TGA scan developed on laminate C-39 after the initial 204C (400F) cure. An approximate 0.8 by 0.8 cm square of composite was cut from the laminate and the TGA profile run at a very slow (0.5C/min) scan rate. The purpose of the slow rate was an attempt to establish baseline data for postcure development studies.

The weight loss rate divides into five distinct segments:

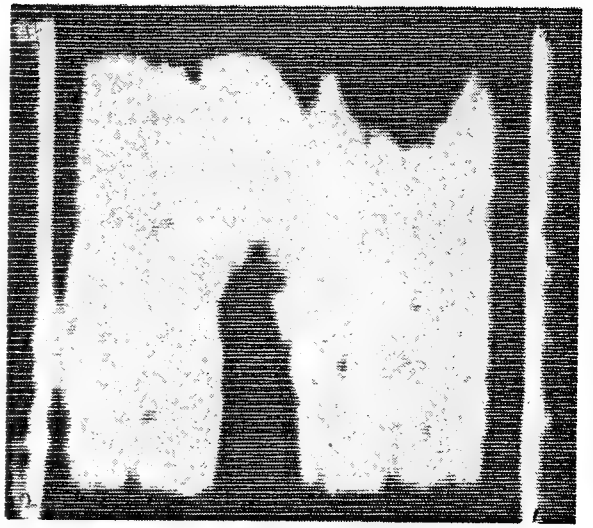
T_1 - 65C (149F) - sorbed moisture loss

T_2 - 215C (419F) - retained solvent (NMP) loss below existing Tg

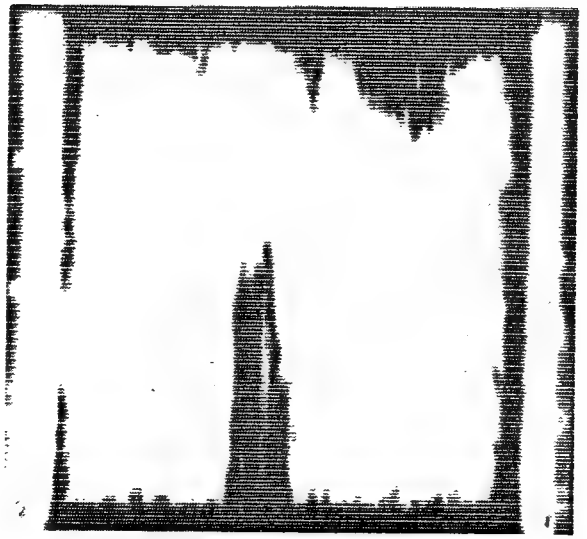
T_3 - 358C (676F) - retained solvent (NMP) loss at or near advancing plasticized Tg



A. FREQUENCY – 1 MHz
GAIN – 1.8



B. FREQUENCY 2.25 MHz
GAIN – 20



C. FREQUENCY – 5 MHz
GAIN – 20

Figure 15. Ultrasonic C-Scan for Laminate C-38

TABLE III

PROPERTIES FOR NR-150B2-S5X GRAPHITE/POLYIMIDE COMPOSITE C-34 TO C-39 (12 PLY, 0°)

Laminate No.	C-34	C-35	C-36	C-37	C-38	C-39
Fiber	Celion 3000	Modmor II	Celion 3000	Modmor II	Celion 3000	Modmor II
Cure	CR-4	CR-4	CR-4	CR-4	CR-4	CR-4
Postcure	STD	STD	None	None	STD-A	None
Flexural Strength MN/m^2 (ksi)						
RT					364-1144 (52-163)	
316C (600F)					—	
Short Beam Shear Strength MN/m^2 (ksi)						
RT					77 (11.0)	
316C (600F)					—	
Specific Gravity					1.47-1.60	
Fiber Content,						
Wgt, %					63.7	
Volume, %					56-59	
Cured Ply Thickness, mm (in)						
Initial Cure	.170 (.0067)	.173 (.0068)	.114 (.0045)	.137 (.0054)	.155 (.0061)	.121 (.0069)
Postcure	.149 (.0059)	—			.151 (.0059)	
Glass Transition Temp., C	355	353			362	
Void, %					.8-8.7	
Wgt. Loss, %						
Cure	12.1	11.6	24.3	26.9	11.5	10.6
Postcure	6.6	8.5			5.2	
Total	18.7	20.1			16.7	
Comments	No flow, Blister	No flow, Blister	Very High Flow	Very High Flow	Slight Flow, Delam	No Flow

TABLE IV

PHYSICAL PROPERTIES OF LAMINATE C-38

Specimen No.	Fiber Volume, %	Specific Gravity	Porosity, %
1	59.2	1.60	0.8
2	56.5	1.58	1.5
3	59.3	1.50	7.0
4	58.2	1.47	8.7

TABLE V

FLEXURAL STRENGTH OF LAMINATE C-38 SPECIMENS VS ULTRASONIC C-SCAN INDICATED DEFECTS

C-Scan Evaluation	Flexural Strength, MN/m^2 (ksi)
Minor Porosity	1141 (163)
Major Porosity	945 (135)
Severe Porosity	798 (114)
Possible Delamination	364 (52)

T_4 - 380C (716F) - retained solvent loss above ultimate Tg

T_5 - 450C (842F) - decomposition

These results were obtained on a laminate that shows essentially no voids prior to the postcure procedure.

The loss of solvent below the 204C (400F) cure temperature is not surprising since the small sample, with its very large surface area at the edges should release residual solvent quite readily.

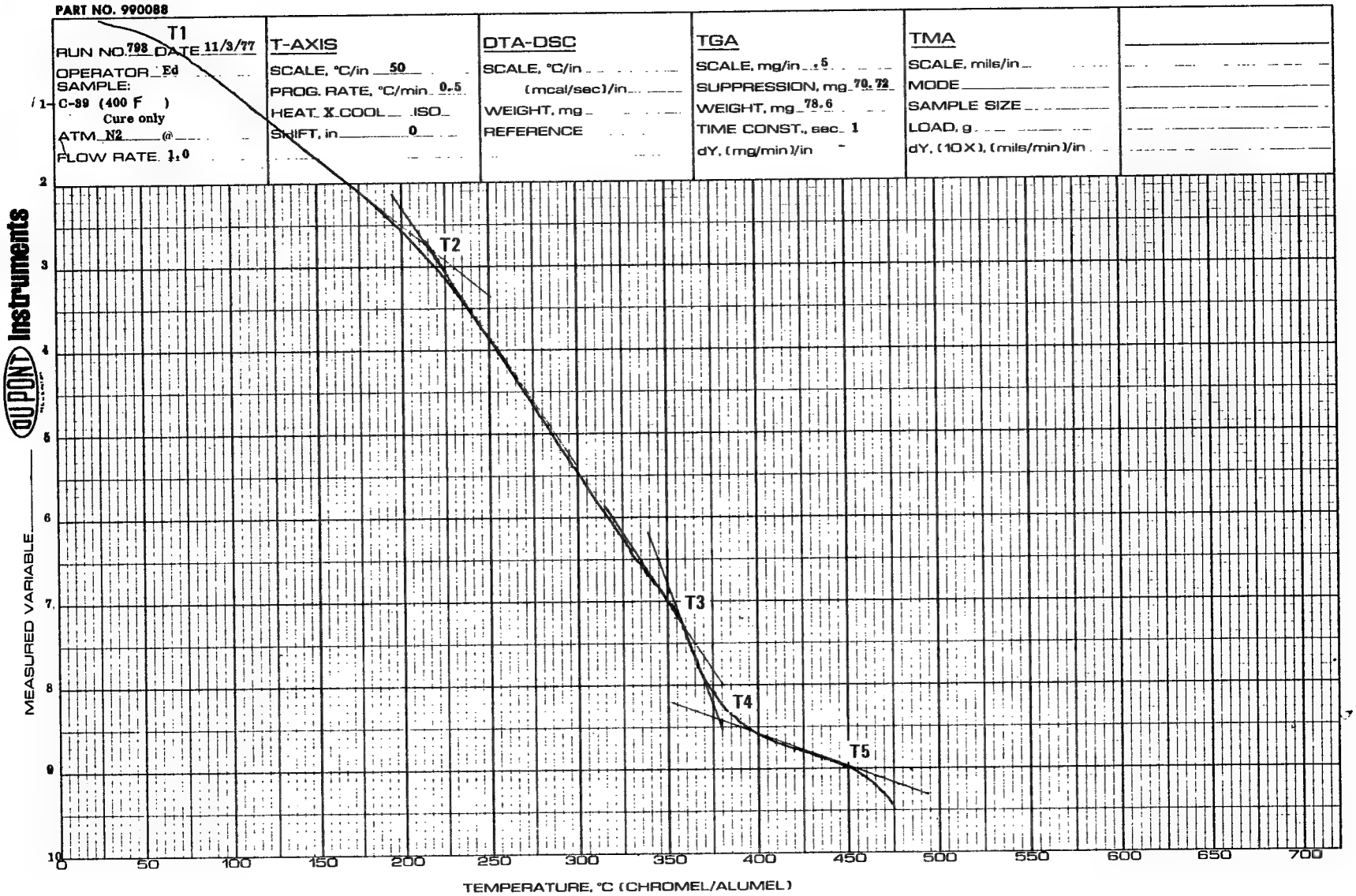


Figure 16. Weight Loss During Postcure by TGA

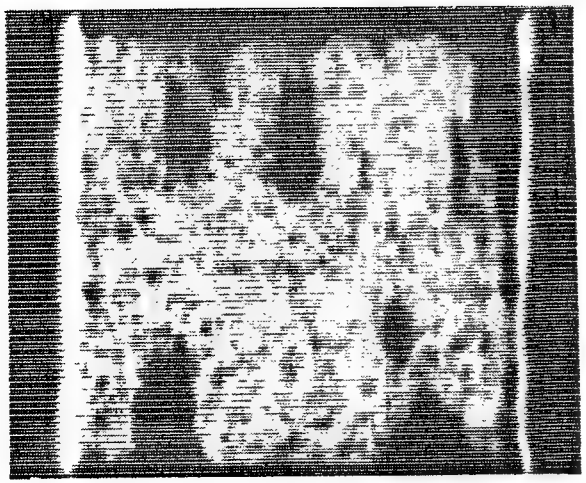
Because of the large edge (fiber ends) surface area, the diffusion rates from the TGA specimen is not representative of an actual laminate. However, the TGA curve represents a model of what is desirable to achieve in a laminate postcure. The heating rate is sufficiently low so as not to exceed the Tg of the plasticized laminate as the solvent is removed.

At this point it became obvious that the postcure schedule, which had been successful with earlier laminates, was not adequate for the laminates presently being fabricated. This is attributed to their very low void content and the fact that the laminates have a higher fiber volume, which results in a longer path for volatile to diffuse to the laminate surface.

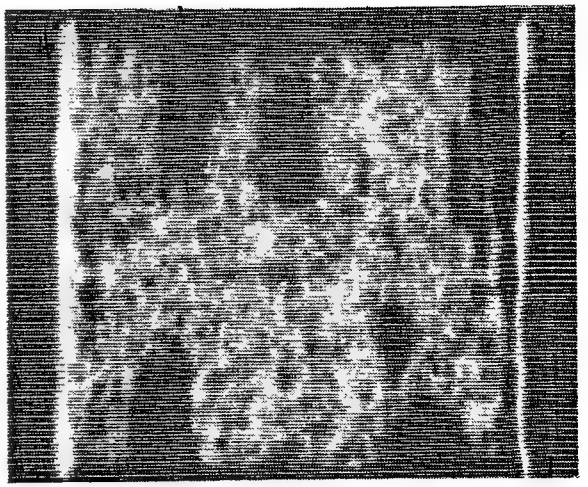
Laminates C-40 (Celion 3000) and C-41 (Modmor II) were prepared using the CR-4 initial cure. Laminate C-40 was postcured by the following modified schedule (Standard B) under 200 psi autoclave pressure:

3 hrs at 288C (550F)
1 hr at 316C (600F)
2 hrs at 343C (650F)
1 hr at 371C (700F)
1 hr at 399C (750F)

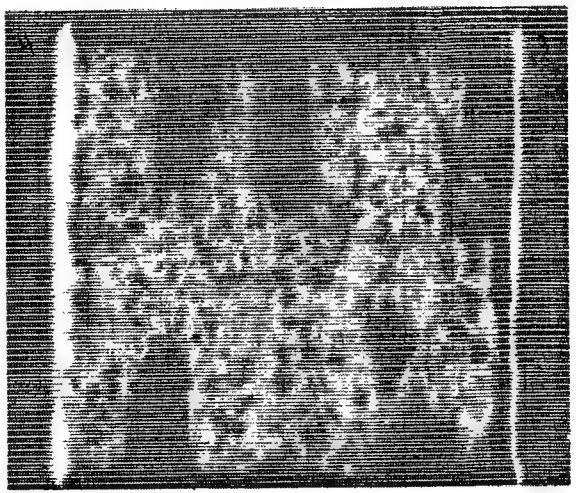
This postcure differed from the standard postcure previously used in that the 3 hr 288C (550F) hold was added, an additional 1 hr hold at 343C (650F) was added and the time at 399C (750F) was decreased from 5 to 1 hr. The rationale for this cycle involved an attempt to remove more of the NMP solvent at lower temperatures. After postcure the laminate was inspected by ultrasonic C-scan at different gain settings at 2.25 MHz (Figure 17). Typically, the C-scan is first conducted at a lower frequency where sound transmission is more readily obtained. If good scans are obtained, inspection is conducted at higher frequencies. In general, a good laminate is indicated



A. GAIN – 3



B. GAIN – 5



C. GAIN – 7

Figure 17. Ultrasonic C-Scans for Laminate C-40 (2.2 MHz)

when uniform dark scans are obtained at high frequency and low gain. The scans for laminate C-40 at 2.25 MHz and all gains indicated delamination and porosity over the majority of the laminate. Mechanical properties were low (Table VI) and, although a void content of approximately 1% was obtained, the specimen was obviously not representative of the laminate. Since Modmor II fiber was no longer available, laminate C-41 was not postcured.

Laminate C-44 (Celion 3000) was prepared by the CR-4 initial cure cycle with an additional two hours at 232C (450F) being added in an attempt to reduce the residual solvent level prior to postcure. The postcure cycle (Standard C) for laminate C-44 involved adding temperature holds at closer intervals for the lower temperature portion of the schedule as follows:

1 hr at 260C (500F)
1 hr at 288C (550F)
1 hr at 316C (600F)
1 hr at 343C (650F)
1 hr at 371C (700F)
5 hrs at 399C (750F)

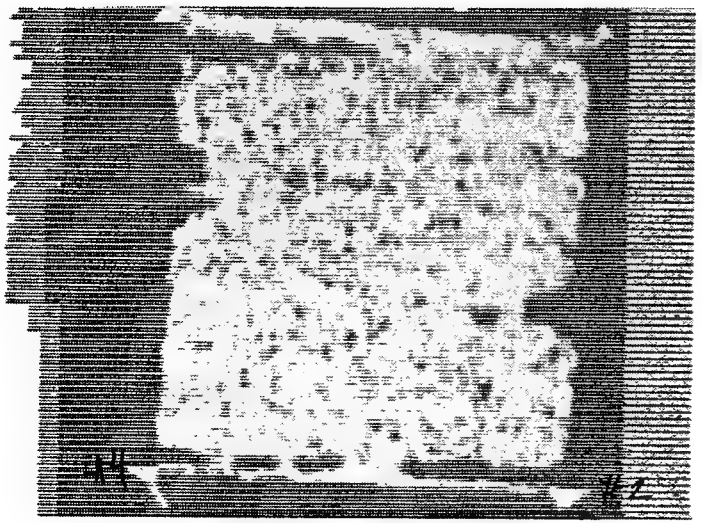
After postcure the laminate was inspected by ultrasonic C-scan at 2.25 and 5 MHz (Figure 18). Scans at 2.25 MHz at gain settings of 10 and 20 indicated uniformity and some porosity. However, the scan at 5 MHz indicated delamination, which was reflected in the low mechanical properties measured (Table VI). For laminate C-45 the CR-4 cure cycle was modified (CR-11) by applying vacuum bag pressure at the beginning of the cure cycle in an attempt to obtain some degree of resin flow and to lower the amount of residual solvent which must be removed during postcure. Excessive flow was experienced resulting in some porosity in the laminate. Figure 19 is the ultrasonic C-scan for laminate C-45 and illustrates the increase in porosity after postcure.

TABLE VI

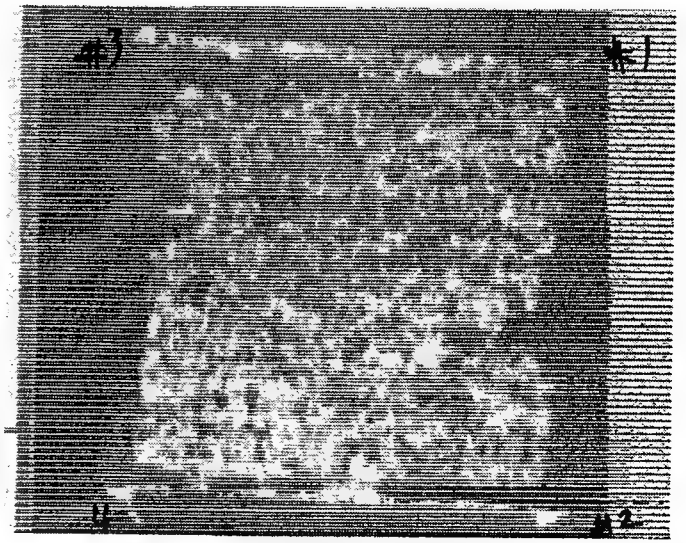
PROPERTIES FOR NR-150B2-S5X GRAPHITE/POLYIMIDE COMPOSITE C-40 TO C-45 (12 PLY, 0°)

Laminate No.	C-40	C-41	C-44	C-45
Fiber	Celion 3000	Modmor II	Celion 3000	Celion 3000
Cure	CR-4	CR-4	CR-4D	CR-11
Postcure	STD-B	—	STD-C	STD-C
Flexural Strength MN/m^2 (ksi)				
RT	1064 (152)	—	714 (102)	1379 (197)
316C (600F)	448 (64)	—	—	721 (103)
Short Beam Shear Strength MN/m^2 (ksi)				
RT	73.5 (10.5)	—	60.9 (8.7)	58.8 (8.4)
316C (600F)	17.5 (2.5)		—	35 (5.0)
Specific Gravity	1.55	—	1.53	1.54
Fiber Content,				
Wgt, %	64.6	—	65.3	78.6
Volume, %	57.5	—	60.1	74.6
Weight Loss, %				
Initial cure	5.6	6.9	6.8	5.2
Postcure	5.9	—	6.8	5.2
Glass Transition Temp., C	322	—	360	350
Void, %	0.6	—	2.1	5.5
Wgt. Loss, %				
Initial cure	12.6	10.2	11.6	26.2
Postcure	8.0		6.7	2.6
Total	20.6		18.3	28.8
Comments	No Flow	No Flow	No Flow	High Flow

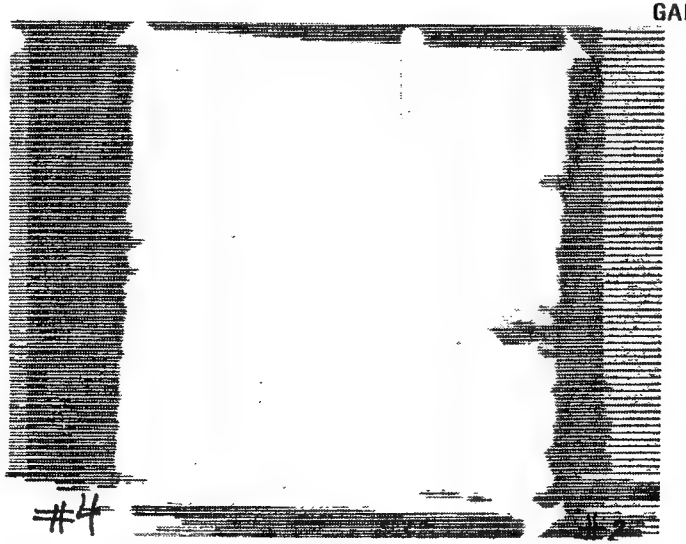
At this point it became apparent that the problem of postcure removal of solvent from the dense thermoplastic NR-150B2 laminate was a very complex one. One approach for achieving a postcure would be to conduct an empirical study that would involve determining weight loss versus time at short temperature intervals over the postcure range. However, this approach would be very time consuming and would



A. FREQUENCY 2.25 MHz
GAIN – 10



B. FREQUENCY 2.25 MHz
GAIN – 20



C. FREQUENCY 5.0
GAIN – 50

Figure 18. Ultrasonic C-Scans for Laminate C-44

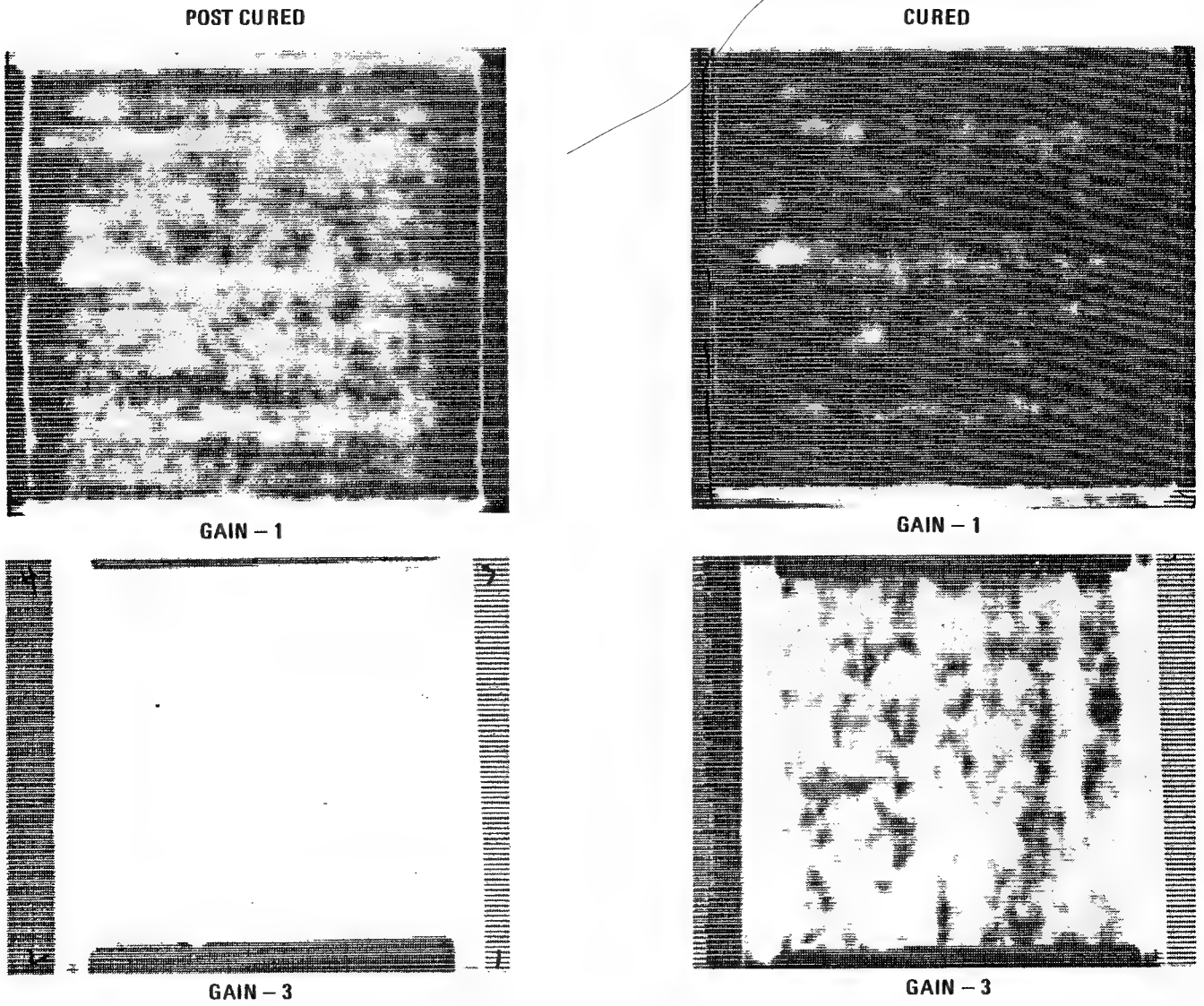


Figure 19. Ultrasonic C-Scans for Laminate C-45 Before and After Postcure (2.25 MHz)

have to be worked out for a variety of laminate thicknesses. The ideal solution to the problem would be an indicator that would provide a signal when the temperature increase rate approaches a point where there is sufficient internal pressure to cause blistering or delamination. If this was possible the temperature rate could be changed or temperature holds could be initiated as the critical temperature is approaching. Molecular activity would be expected to increase as the laminate approaches blistering temperature and should be reflected in the dielectric properties of the material, which can be measured by a dielectric cure monitor. Certainly the temperature at which blistering occurs should be indicated (capacitance change) and provide information as to temperatures for initiating holds. Future efforts will investigate this approach for developing an optimized postcure.

2.4 ADHESIVE BONDING

All materials have been received for formulating adhesives for evaluation. Evaluation will be initiated as soon as the laminate postcure problem has been resolved and satisfactory adherent can be fabricated.

2.5 CHOPPED FIBER MOLDING

The problem of removing residual NMP from thick, high-pressure molding is considered a major difficulty with NR-150B2, which severely limits its application. The use of Dyglyme solvent in lieu of NMP was considered a viable approach for alleviating this problem. Dyglyme has been used successfully by DuPont for adhesive bonding with NR-150 polyimide. A purchase order for a five-pound quantity of NR-150B2/Dyglyme prepreg had been issued to Fiberite with the intent of chopping the material to give a molding compound. However, as a result of concern by both DuPont and Fiberite in being successful in prepregging with the resin solution, the procurement was cancelled. A preliminary in-house evaluation will be conducted to appraise the potential of this approach and better define the prepreg preparation conditions and characteristics.

SECTION 3

FUTURE ACTIVITIES

The primary activity during the next reporting period will involve development of a satisfactory postcure for the NR-150B2 composites, using the dielectric cure monitor to establish time/temperature conditions.

Tooling will be developed for the stiffened panel task and fabrication and testing will be initiated as satisfactory laminates are produced.

Adhesive bonding efforts will involve formulation studies and adhesive film development. Fabrication and testing of adhesive bonded composite specimens will be initiated when satisfactory composite adherents are obtained.

The chopped fiber molding study will involve evaluation of prepregging and molding parameters using NR-150B2 bond on Dyglyme and NMP solvent.

SECTION 4

SCHEDULE AND COST

The schedule (Figure 20) has been revised to reflect the problem experienced in post-cure development. Resolution of this problem during the next reporting period will allow completion of the program as originally scheduled by conducting certain of the task in parallel.

The actual cost curve continues to underrun the original projected cost curve (Figure 21) because a number of tasks have not been initiated due to the postcure problem. A new budget and projected expenditure cure will be developed once the postcure problem has been resolved.

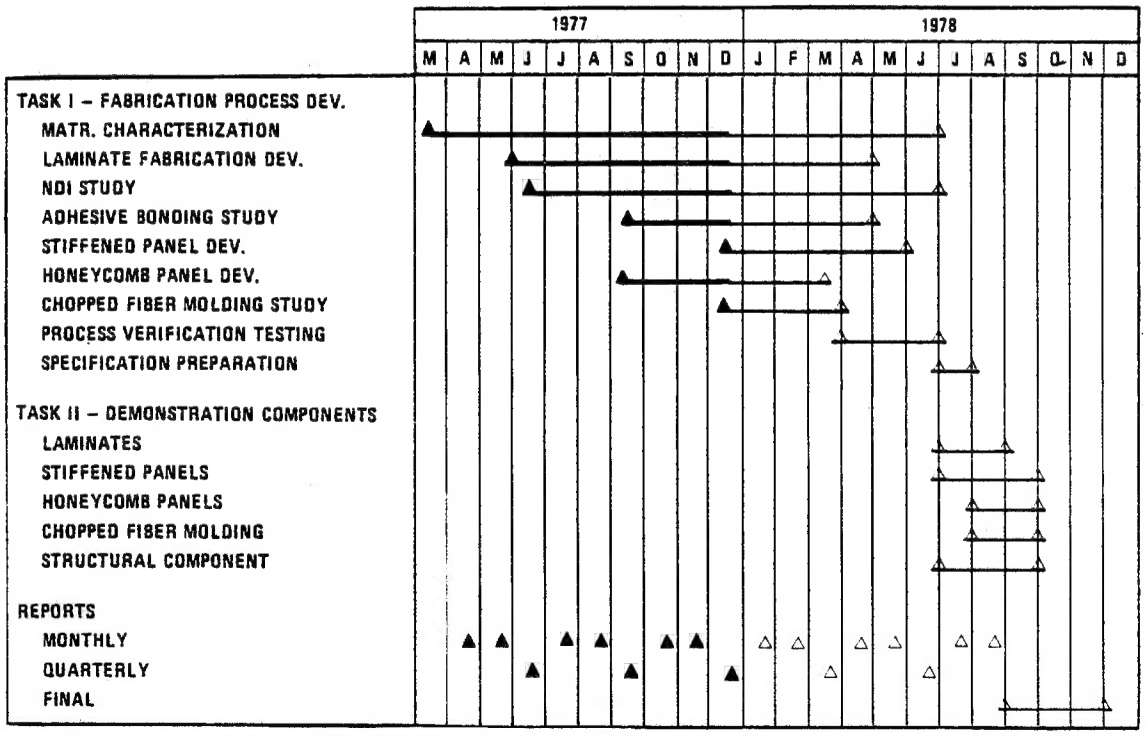


Figure 20. Schedule

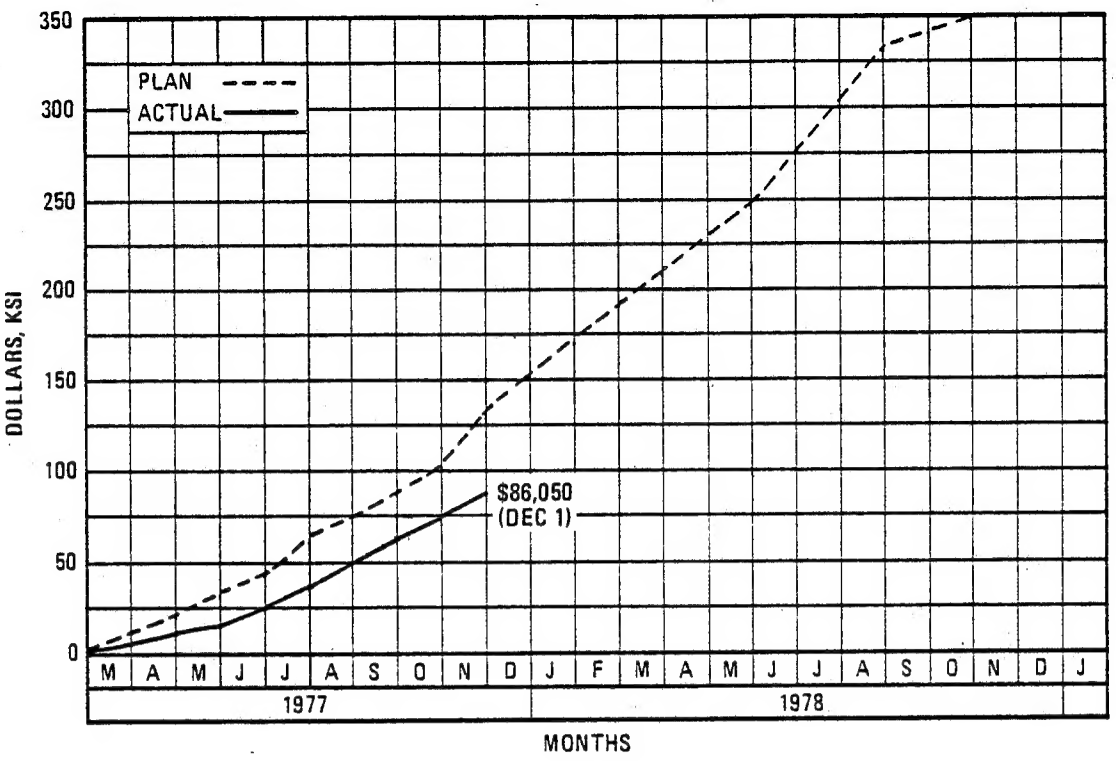


Figure 21. Cost